Factors Affecting Whether a Process is Spontaneous

1. There are two factors that determine whether a reaction is spontaneous. They are the enthalpy change and the entropy change of the system.

a. The enthalpy change, ∆H, is the difference in the sum of the internal energy and PV work energy of the reactants to the products.

b. The entropy change, ∆S, is the difference in randomness of the reactants compared to the products.

2. Enthalpy

∆H generally measured in kJ/mol

a. Stronger bonds = more stable molecules

b. A reaction is generally exothermic if the bonds in the products are stronger than the bonds in the reactants.

c. Exothermic = energy released; ∆H is negative.

d. A reaction is generally endothermic if the bonds in the products are weaker than the bonds in the reactants.

e. Endothermic = energy absorbed; ∆H is positive.

The enthalpy change is favorable for exothermic reactions and unfavorable for endothermic reactions.

3. Entropy

a. ∆S generally measure in J/mol

a process where the final condition is more random than the initial condition, **D*S*system is positive** and the **entropy change is favorable for the process to be spontaneous**.

For a process where the final condition is more orderly than the initial condition, **D*S*system is negative** and the **entropy change is unfavorable for the process to be spontaneous**.

4. Second Law of Thermodynamics

The second law of thermodynamics says that the total entropy change of the universe must be positive for a process to be spontaneous.

For reversible process ∆Suniverse = 0

For irreversible (spontaneous) process ∆Suniverse > 0

∆Suniverse = ∆Ssystem + ∆Ssurroundings

If the entropy of the system decreases, then the entropy of the surroundings must increase by a larger amount.

When ∆Ssystem is negative, ∆Ssurroundings must be positive and big for a spontaneous process.

When ice is placed in water, heat flows from the water into the ice. According to the second law, heat must flow from water to ice because it results in more dispersal of heat. The entropy of the universe increases.



5. The second law demands that the entropy of the universe increase for a spontaneous process.

Yet processes like water vapor condensing are spontaneous, even though the water vapor is more random than the liquid water. Gas 🡪Liquid ∆S = negative

If a process is spontaneous, yet the entropy change of the process is unfavorable, there must have been a large increase in the entropy of the surroundings.

The entropy increase must come from heat released by the system; the process must be exothermic.

Gas 🡪 Liquid ∆H = negative; it’s an exothermic process.

6. Third Law of Thermodynamics The absolute entropy of a substance is the amount of energy it has due to dispersion of energy through its particles.

The third law states that for a perfect crystal at absolute zero, the absolute entropy = 0 J/mol ∙ K.

Therefore, every substance that is not a perfect crystal at absolute zero has some energy from entropy.

Therefore, the absolute entropy of substances is always positive